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㊹発明の名称　基板洗浄方法

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movable nozzle
spray
hot sulfuric + ozone
typ. appl. 120°C

明　細　書

1. 発明の名称

基板洗浄方法

2. 特許請求の範囲

1. オゾン含有雰囲気内に所定処理温度に加熱された被洗浄基板を配設し、該被洗浄基板面を前記オゾンと反応させる工程、及び

前記被洗浄基板面に熱硫酸あるいはオゾン含有水添加の熱硫酸を噴射する工程を含むことを特徴とする基板洗浄方法。

2. 前記オゾン含有雰囲気中のオゾン含有率が30重量%以下であることを特徴とする請求項1記載の方法。

3. 熱硫酸と微少オゾン含有水とを洗浄液として洗浄槽に供給しながら、前記洗浄液内に被洗浄基板を配設することを特徴とする基板洗浄方法。

3. 発明の詳細な説明

〔概　要〕

基板洗浄方法に係り、特にオゾンと硫酸を用いて半導体ウェハを洗浄する方法に関し、

一定条件下に管理された基板洗浄方法を提供することを目的とし、

オゾン含有雰囲気内に所定処理温度に加熱された被洗浄基板を配設し、該被洗浄基板面を前記オゾンと反応させる工程、及び前記被洗浄基板面に熱硫酸あるいはオゾン含有水添加熱硫酸を噴射する工程を含むこと、及び熱硫酸と微少オゾン含有水とを洗浄液として洗浄槽に供給しながら、前記洗浄液内に被洗浄基板を配設することを構成とする。

〔産業上の利用分野〕

本発明は基板洗浄方法に係り、特にオゾンと硫酸を用いて半導体ウェハを洗浄する方法に関するものである。

〔従来の技術〕

従来、半導体装置を製造する工程において、半導体基板（例えばシリコンウェハ）を硫酸と過酸化水素との混合液からなる洗浄液によって洗浄す

る方法が知られている。

〔発明が解決しようとする課題〕

過酸化水素は撹拌や循環等の外力に対して自己分解活性が高く混合薬液の純度や液温等に影響を与え、洗浄されるウェハの清浄度が低下した。また自己分解活性によって不足した過酸化水素を補給した際にその混合薬液の濃度管理に問題があった。従って常に一定条件下に管理された処理薬液（洗浄液）を保有することが出来ず、薬液を頻繁に取り替えなければならないために長い調整時間と多量の薬液を消費していた。

本発明は一定条件下に管理された基板洗浄方法を提供することを目的とする。

〔課題を解決するための手段〕

上課題は本発明によればオゾン含有雰囲気内に所定処理温度に加熱された被洗浄基板を配設し、該被洗浄基板面を前記オゾンと反応させる工程、及び

前記被洗浄基板面に熱硫酸あるいはオゾン含有水添加熱硫酸を噴射する工程を含むことを特徴とする基板洗浄方法によって解決される。

本発明では上記オゾン含有雰囲気中のオゾン含有率が30重量%以下であることが微量の有機物との接触による爆発の可能性の理由から好ましい。

更に上課題は本発明によれば、熱硫酸と微少オゾン含有水とを洗浄液として洗浄槽に供給しながら、前記洗浄液内に被洗浄基板を配設することを特徴とする基板洗浄方法によって解決される。

本発明で用いる基板としてはシリコンウェハ等がよく用いられる。

本発明で使用された熱硫酸は循環経路内のフィルターにより濾過され濃度調整後、再利用される。

〔作　用〕

本発明によれば処理槽内でのウェハの周囲をオゾンが常に存在している状態であり、更に処理槽内は洗浄処理に用いられる温度に維持している為、ウェハ表面の有機物を酸化し又外部からの汚染物から切り離れている状態で常に一定条件の表面状態を維持するウェハが得られる。

〔実施例〕

以下本発明の実施例を図面に基づいて説明する。

第1図は本発明の一実施例を示す模式図である。

第1図において、30重量%以下のオゾン（O_3）雰囲気1内の石英洗浄処理槽2にヒーター3によって約120℃に予熱された複数のウェハ4（一枚のみ示す）を配置し、オゾン独自の有機物酸化能力（酸素ラジカル）によりウェハ表面上の有機物の酸化を促進する。その後、オゾンの雰囲気濃度が数重量%以下迄消費された時点でウェハ4間のほゞ中央に配設されたノズルから各ウェハの両面に熱硫酸又はオゾン含有水添加の熱硫酸が噴霧される。この場合熱硫酸噴射11のためのノズル10は可動式である。

洗浄に用いられた熱硫酸、オゾン含有水等はウェハ表面に付着していた有機物と共にポンプ5aによって底部から排出されフィルター7によって浄化される。熱硫酸槽とフィルター7間にはオゾン含有水槽6が、そしてフィルター7とポンプ5bの間には熱硫酸槽8が設けられている。

第2図は、本発明の他の実施例を説明するための模式図である。

第2図には熱硫酸とオゾン含有水の混合液（洗浄液）12を収容した石英からなる洗浄処理槽2が示されている。

3は洗浄液加熱用ヒータ、5は洗浄液を循環させるためのポンプ、5は洗浄によって落された有機物粒子等を濾過するためのフィルター、6はオゾン含有水槽である。

ウェハ洗浄処理槽1は約25ℓの洗浄液が収容されておりその内部にウェハ4を浸漬して洗浄される。ウェハに付着しているごみ、例えば有機物は約120℃に加熱された硫酸とオゾンとの反応で生じた炭化オゾン分解酸素ラジカルでCOに変換され除去される。万一有機物が残存しても循環系内のフィルター7によって捕獲された。本実施例では微少オゾン供給を水と共にすなわちオゾン含有

水の形態をとって行い、硫酸から蒸発消失する水分の補給を行うことが可能となり一定の硫酸濃度約96%を保持できた。

〔発明の効果〕

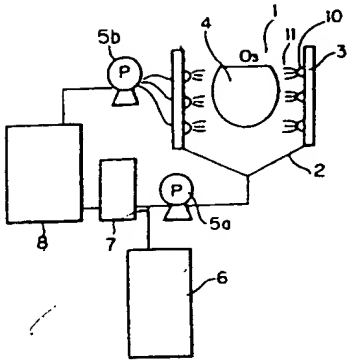
以上説明した様に本発明によれば、ユースポイント内でウェハの周囲はオゾンが常に存在している状態である為、ウェハ表面の有機物の酸化と促進と外部からの汚染を断っている状態であり、常に一定条件の表面を持つウェハを得ることができる。

4. 図面の簡単な説明

第1図は本発明の一実施例を示す模式図であり、

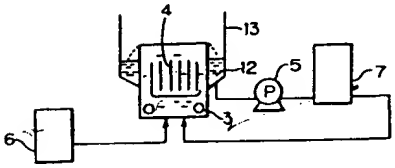
第2図は本発明の他の実施例を示す模式図である。

1…オゾン雰囲気、　2…洗浄処理槽、
3…ヒーター、　4…ウェハ、
5a・5b…ポンプ、　6…オゾン含有水槽、
7…フィルター、　8…熱硫酸。



1… オゾン雰囲気
2… 洗浄処理槽
3… ヒーター
4… ウェハ
5a,5b … ポンプ
6 … オゾン含有水槽
7 … フィルター
8 … 熱硫酸槽
10 … ノズル
11 … 熱硫酸噴射
12 … 洗浄液
13 … 洗浄槽

第 1 図



第 2 図

CLIPPEDIMAGE= JP404125927A
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TITLE: METHOD OF WASHING SUBSTRATE

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ABSTRACT:
PURPOSE: To obtain a wafer having always a surface of a constant condition, by arranging a wafer heated at a specified treatment temperature in an ozone-containing atmosphere, and letting hot sulfuric acid or hot sulfuric acid to which ozone-containing-water is added, after reaction with ozone.

CONSTITUTION: A wafer 4 preheated by a heater 3 is arranged in a washing treatment tank 2 made of quartz in an ozone atmosphere 1, and the oxidizing of organic matter on the wafer surface is promoted. The ozone content is set lower than or equal to 30wt.%. From nozzles 10, hot sulfuric acid or hot sulfuric acid to which ozone-containing-water is added is sprayed on both surfaces of the wafer . The hot sulfuric acid and the like which have been used for washing are discharged from the bottom part by using a pump 5a, together with organic matter which has stuck on the surface, and cleaned with a filter 7 for circulation. The ozone-containing-water is supplied from an ozone-containing- water tank 6.

			Document ID	Issue Date	Pages	Title
390	☐	☐	JP 04114787 A	19920415	16	TREATMENT OF WATER TO BE TREATED
391	☐	☐	JP 04114431 A	19920415	2	OXIDIZATION PROCESS

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25. Specifications

26. Title of the Invention

27. Method for Washing Substrate

28. Claims

29. A method for washing a substrate that is characterized by: a process by which a substrate that has been pre-heated to a specified treatment temperature is arranged within an atmosphere

containing ozone such that the surface of the substrate is allowed to react with the ozone; as well as a process by which the surface of the aforementioned substrate is sprayed with hot sulfuric acid or a form of hot sulfuric acid in which water containing ozone has been added.

30. A method noted in Claim 1 that is characterized by the fact that the maximum percentage of ozone included within the aforementioned ozone atmosphere is 30 wt.%.

31. A method for washing a substrate that is characterized by the fact that a cleaning solution made from water containing sulfuric acid and a small amount of ozone is delivered into a cleaning tank while the substrate to be washed is placed within the aforementioned cleaning solution.

32. Detailed Explanation of the Invention

33. (Summary)

34. This invention is related to a method for washing a substrate, particularly a method in which a semiconductor wafer is washed using ozone and sulfuric acid. The objective of this invention is to provide a method for washing a substrate in which the process is controlled under set conditions.

35. The method for washing a substrate according to this invention is composed of the following: a process by which a substrate that has been pre-heated to a specified treatment temperature is arranged within an atmosphere containing ozone such that the surface of the substrate is allowed to react with the ozone; a process by which the surface of the aforementioned substrate is sprayed with hot sulfuric acid or a form of hot sulfuric acid in which water containing ozone has been added; and a cleaning solution that is made from water containing sulfuric acid and a small amount of ozone and is delivered into a cleaning tank while the substrate to be washed is placed within the aforementioned cleaning solution.

36. (Industrial Field of Application)

37. This invention is related to a method for washing a substrate, particularly a method in which a semiconductor wafer is washed using ozone and sulfuric acid.

38. (Prior Art)

39. In previous processes in which semiconductor devices are manufactured, a known method is used in which the semiconductor substrates (e.g., silicon wafers) are washed in a cleaning solution that is a mixed liquid containing sulfuric acid and hydrogen peroxide.

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41. (Problem to Be Solved by the Invention)

42. When an external force such as a stirring or circulating action is applied to hydrogen peroxide, a high level of self-degradation activity occurs, which has an effect on the purity and liquid temperature of a mixed chemical and results in a drop in the cleanliness of the wafer that is to be washed. Also, when a solution is supplemented with hydrogen peroxide that has been made inferior as a result of self-degradation activity, this poses a problem from the standpoint of controlling the concentration of a mixed chemical. Therefore, it usually becomes impossible to obtain a treatment chemical (cleaning solution) that is controlled under set conditions. This in turn makes it necessary to frequently replace the solution, which requires a significant amount of adjustment time and consumes a large quantity of solution.

43. The objective of this invention is to provide a method for washing a substrate in which the process is controlled under set conditions.

44. (Means for Solving the Problem)

45. The problem noted above can be solved through the use of this invention, which is a method for washing a substrate that is characterized by: a process by which a substrate that has been pre-heated to a specified treatment temperature is arranged within an atmosphere containing ozone such that the surface of the substrate is allowed to react with the ozone; as well as a process by which the surface of the aforementioned substrate is sprayed with hot sulfuric acid or a form of hot sulfuric acid in which water containing ozone has been added.

46. The reason that this invention calls for a preferred maximum percentage of ozone included within the aforementioned ozone atmosphere of 30 wt.% is due to the possibility of explosion upon contact with small amounts of organic material.

47. In addition, this invention solves the problem noted above due to the fact that this method for washing a substrate is characterized by a cleaning solution that is made from water containing sulfuric acid and a small amount of ozone and is delivered into a cleaning tank while the substrate to be washed is placed within the aforementioned cleaning solution.

48. Substrates often used in the case of this invention include silicon wafers, etc.

49. The hot sulfuric acid used in this invention is sent through a filter located within the flow circuit, after which the concentration is adjusted and the sulfuric acid is reused.

50. (Operation)

51. According to this invention, ozone constantly surrounds the wafer within the treatment tank, and since the inside of the treatment tank is maintained at a temperature for the cleaning treatment, the wafer is separated from organic material on the wafer surface or any contaminants from the outside, making it possible to obtain a wafer in which the surface condition is maintained at a constant state.

52. (Embodiments)

53. The following is an explanation of an embodiment of this invention using drawings.

54. Figure 1 is a model drawing that illustrates an embodiment of this invention.

55. In Figure 1, multiple wafers 4 (only one shown) are arranged which have been pre-heated to approximately 120°C using a heater 3 within a quartz cleaning treatment tank 2 with a maximum ozone (O_3) atmosphere of 30 wt.%. Inside the tank, oxidation of the organic material on the wafer surface is promoted by the organic material oxidation capability (oxygen radicals) of the ozone itself. Then, at a point at which the atmospheric concentration of the ozone is consumed to a certain maximum weight percentage, nozzles that are positioned approximately in the center between the wafers 4 spray hot sulfuric acid, or a form

of hot sulfuric acid in which water containing ozone has been added, onto the wafer surface. In this case, the nozzles 10 for the hot sulfuric acid spray 11 are movable.

56. The sulfuric acid, water containing ozone, etc., that are used in the cleaning process are sent out from the bottom of the tank, along with the organic material that was stuck to the surface of the wafers, through the use of a pump 5, and a filter 7 is used for purification. A tank 6 for the water containing the ozone is located between the hot sulfuric acid tank and the filter 7, and the hot sulfuric acid tank 8 is located between the filter 7 and the pump 5b.

57. Figure 2 is a model drawing that is used to explain another embodiment of this invention.

58. Figure 2 shows a cleaning treatment tank 2 that is made of quartz and contains a mixed solution (cleaning solution) 12 of hot sulfuric acid and water containing ozone.

59. Item 3 is a heater that is used to heat the cleaning solution, item 5 is a pump that is used to circulate the cleaning solution, item 5 [sic; should be item 7] is a filter that is used to remove organic particles that fall off during the cleaning process, and item 6 is the tank that holds the water containing the ozone.

60. The wafer cleaning treatment tank 1 contains approximately 25 liters of cleaning solution, and the wafers 4 are submerged into this tank in order to be cleaned. Dirt particles, such as organic material, that are stuck to the wafers are converted to CO by the decomposition oxygen radicals of the carbonated ozone that is generated by the reaction between the sulfuric acid and the ozone when they are heated to a temperature of approximately 120°C. After this material is converted to CO, it is then discarded. Even if organic material remains, it will be captured by the filter 7 within the circulation system.

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62. According to this embodiment, [it] will take on the form of small amounts of ozone delivered along with water, namely the water containing ozone, and this makes it possible to supplement the water amount that is lost through evaporation from the sulfuric acid, resulting in the ability to maintain a constant sulfuric acid concentration of approximately 96%.

63. (Result of the Invention)

64. As explained above, this invention provides a condition in which ozone continuously surrounds the wafers, which in turn provides a condition in which oxidation of organic material is promoted along the wafer surface and outside contaminants are removed, making it possible to obtain a wafer in which the surface is maintained at a constant state.

65. Simple Explanation of the Drawings

66. Figure 1 is a model drawing that shows an embodiment of this invention.

67. Figure 2 is a model drawing that shows another embodiment of this invention.

68. 1: Ozone atmosphere

69. 2: Cleaning treatment tank

70. 3: Heater

71. 4: Wafers

72. 5a, 5b: Pumps

73. 6: Tank for water containing ozone

74. 7: Filter

75. 8: Hot sulfuric acid tank

Figure 1

Figure 2

76. 1: Ozone atmosphere

77. 2: Cleaning treatment tank

78. 3: Heater

79. 4: Wafers

80. 5a, 5b: Pumps

81. 6: Tank for water containing ozone

82. 7: Filter

83. 8: Hot sulfuric acid tank

84. 10: Nozzles

85. 11: Hot sulfuric acid spray

86. 12: Cleaning solution

87. 13: Cleaning tank

88. -135-